

SPECIFICATION

ULTRA FINE GRAIN STEEL HAVING NITRIDE LAYER

Technical Field

The present invention relates to an ultra fine grain steel having a nitride layer. More particularly, the present invention relates to an ultra fine grain steel having a nitride layer that is formed without adding alloy elements such as Cr and Mo, which are expensive and detrimental at the time of recycling and to the steel whose fatigue strength is enhanced.

Background Art

In a metal part such as a rotary shaft that receives a bending stress and a twisting stress, a fatigue crack is generated in a surface subjected to high stress and the metal part is finally brought to fatigue fracture. For this reason, hardening of a surface and thereby imparting high fatigue strength to the surface is effective for imparting high fatigue strength to an entire metal part. Moreover, to harden a surface is also effective from a viewpoint of wear resistance and corrosion resistance. This is similar to an ultra fine grain steel having high strength and high toughness in which ferrite grains are extremely small in size (for example, see patent document 1).

Conventionally, in order to harden a surface, nitrifying of a surface has been thought to be effective but in order to nitride a surface, it is necessary to produce nitrides of alloy elements such as Cr, Mo, Ti, or Nb by adding the alloy elements and by holding temperatures from 450 °C to 590 °C for from 0.5 to 100 hours (for example, see non-patent document 1). Actually, when pure iron is nitrified by use of ammonia gas, an iron nitride film having a thickness of several

μm to several tens μm is only formed on a surface and hardness of surface becomes, at most, about 250 Hv. Iron nitride hardly precipitates inside or even if an iron nitride slightly precipitates, the iron nitride hardly contributes to hardening of a surface.

Since the alloy elements such as Cr and Mo are expensive and are detrimental at the time of recycling, it is desirable to avoid addition of the alloy elements.

The present invention has been made in view of these circumstances. An object of the present invention is to provide an ultra fine grain steel having a nitride layer that is formed without adding alloy elements such as Cr and Mo, which are expensive and detrimental at the time of recycling, and the steel whose fatigue strength is enhanced.

Patent document 1: Japanese Patent Publication No. 2000-309850

Non-patent document 1: Doctoral Dissertation, Hideyuki Kuwahara, November in 1992, Kyoto University

Disclosure of the Invention

The present invention provides an ultra fine grain steel having a nitride layer, wherein the steel has a ferrite grain structure having an average grain size of 3 μm or less and a nitride layer is formed on a surface of the steel (claim 1).

Further, the present invention provides the following modes: grain growth at the time of nitrifying is suppressed by precipitation of carbide or addition of a solid solute element or both (claim 2); the amount of C is 0.01 mass % or more (claim 3); at least one element selected from the group consisting of Mn, Cr, Mo, Ti, Nb, V and P is added (claim 4); the amount of Mn is 0.4 mass % or more (claim 5); the amount of P is 0.035 mass % or more (claim 6); the steel is a carbon steel and the total amount of Cr, Mo, Ti, Nb, and V is 0.1 mass % or less (claim 7); a fatigue

limit is 1.6 times larger than Vickers hardness of a base material (claim 8); a molded part, a part, or a member which is formed from an ultra fine grain steel having a nitride layer as described above (claim 9).

Hereafter, an ultra fine grain steel having a nitride layer of the present invention will be described in more detail while showing embodiments.

Brief Description of the Drawings

Fig. 1 is an FE-SEM photograph showing a nitride layer structure of a Fe-C-Mn coarse grain steel containing 0.002 mass % C that was nitrified by plasma under a condition of $550\text{ }^{\circ}\text{C} \times 26\text{ hours}$.

Fig. 2 is a bar graph showing Vickers hardness of a raw material and a surface of nitride layer, which was formed by plasma under a condition of $550\text{ }^{\circ}\text{C} \times 26\text{ hours}$, of a Fe-C-Mn coarse grain steel containing 0.002 mass % C and a Fe-C-Mn ultra fine grain steel containing 0.05 % C.

Fig. 3 is a graph showing hardness distribution after nitrifying with respect to a fatigue test piece of a Fe-C-Mn ultra fine grain steel containing 0.05 mass % C.

Fig. 4 is an FE-SEM photograph showing a matrix structure after nitrifying of a Fe-C-Mn ultra fine steel containing 0.05 mass % C that was nitrified by plasma under a condition of $550\text{ }^{\circ}\text{C} \times 26\text{ hours}$.

Fig. 5 is a graph showing hardness distribution after nitrifying of a Fe-C-Mn-Si coarse grain steel containing 0.25 mass % C and 0.37 mass % Mn that was nitrified by plasma under a condition of $500\text{ }^{\circ}\text{C} \times 16\text{ hours}$.

Fig. 6 is a graph showing hardness distribution after nitrifying of a Fe-C-Mn-Si coarse grain steel containing 0.45 mass % C and 0.83 mass % Mn that was nitrified by plasma under a condition of $500\text{ }^{\circ}\text{C} \times 16\text{ hours}$.

Fig. 7 is a graph showing results of fatigue tests of a raw material and a nitrified material of a Fe-C-Mn ultra fine grain steel containing 0.05 mass % C in

comparison with each other.

Fig. 8 is a graph showing a grain growth suppressing effect by Fe_3C of a Fe-C-Mn-Si ultra fine steel.

Figs. 9(a) and 9(b) are FE-SEM photographs showing a base metal structure before nitrifying of a Fe-C-Mn-Si ultra fine grain steel containing 0.15 mass % C and a Fe-C-Mn-Si ultra fine grain steel containing 0.45 mass % C, respectively.

Fig. 10 is a graph showing a grain growth suppressing effect with respect to a Fe-C-Mn-Si ultra fine grain steel containing 0.15 mass % C and 0.1 mass % P

Fig. 11 is a graph showing hardness distribution after nitrifying of a Fe-C-Mn-Si ultra fine grain containing 0.45 mass % C and 0.1 mass % P.

Best Mode for Carrying Out the Invention

When an ultra fine steel having a simple composition and a ferrite grain structure having an average grain size of $3\text{ }\mu\text{m}$ or less is held in an ammonia gas atmosphere or an atmosphere containing ammonia gas at temperatures from $450\text{ }^{\circ}\text{C}$ to $590\text{ }^{\circ}\text{C}$ for from 0.5 to 100 hours, a nitride layer is formed on a surface, hardening of the surface occurs, and high fatigue strength is obtained.

Here, a ferrite grain structure means a structure in which ferrite grains are predominant. In this meaning, a ferrite grain structure may be a ferrite single phase structure or may contain carbide, pearlite, martensite, and austenite as a second phase.

In an ultra fine grain steel having a nitride layer in accordance with the present invention, it is preferable that the amount of Mn is 0.4 mass % or more. In a Fe-C-Mn or Fe-C-Mn-Si ultra fine grain steel containing 0.37 mass % Mn, by nitrifying under a condition of $500\text{ }^{\circ}\text{C}$, 16 hours, a surface is hardened but a deep hardened layer is hardly formed. In a case where the amount of Mn is 0.83

mass %, a surface of an ultra fine grain steel is hardened and a deep nitride layer is formed. By the way, in an ordinary steel, Mn of 0.4 mass % is added to at the minimum as measures against MnS. In consideration of the above-described circumstances, it is desirable that the amount of Mn is 0.4 mass % or more in an ultra fine grain steel having a nitride layer in accordance with the present invention.

In an ultra fine grain steel containing C from 0.05 mass % to 0.15 mass %, when the steel is held at temperatures around 550 °C for a long time, grains grow and an ultra fine grain structure is apt to collapse. Grain growth can be prevented or suppressed by increasing the amount of C to precipitate carbide such as Fe_3C , NbC , and TiC , or by adding a solid solution element such as P (phosphor) and V (vanadium), or by both of them. For example, nitrifying can be performed at temperatures around 500 °C for as long a time as 26 hours. By this long-time nitrifying, a deeper nitride layer effective for high fatigue strength is formed. The preferable amount of C is 0.05 mass % or more and the amount of P is preferably 0.035 mass % or more.

Usually, the thickness of a layer hardened by nitrifying, that is, a nitride layer is from 0.5 mm to 1.0 mm in view of fatigue, and in the case of hardening a surface sufficiently, in a coarse grain steel, fatigue fracture occurs in a matrix just below the nitride layer. The fatigue strength of an entire nitrified material is generally determined by strength determined from stress at a starting point of fatigue fracture and the fatigue strength of a matrix. However, in an ultra fine grain steel having a nitride layer in accordance with the present invention, fatigue strength extremely higher than fatigue strength expected from the above-described law is obtained. This is because a nitride layer formed in an ultra fine grain steel by nitrifying is hardened more heavily than the nitride layer of a coarse grain steel. Therefore, an ultra fine grain steel not only has high strength and high toughness

but also has high fatigue strength by nitrifying.

Increasing surface hardness leads to enhancing wear resistance. That is, large compressive stress is given to a nitride layer and remaining compressive stress cancels tensile stress caused by sliding to relatively reduce the tensile stress applied to a surface of an ultra fine grain steel. Moreover, in an ultra fine grain steel in accordance with the present invention, grain growth is prevented or suppressed at nitrifying temperatures and hence properties are less prone to be degraded by heat generated by friction. Therefore, an ultra fine grain steel having a nitride layer in accordance with the present invention shows excellent wear resistance.

An ultra fine grain steel having a nitride layer in accordance with the present invention can be formed in the shape of a bulk or powder.

When a Fe-C-Mn or Fe-C-Mn-Si steel powder is nitrified, the powder shows the same strength as a nitride layer formed on a bulk of an ultra fine grain steel. Therefore, a bulk obtained by sintering nitride powders can become a high-strength material. In this case, sintering can be performed in an atmosphere, which includes single gas of nitrogen gas or ammonia gas, or a mixture of them, or either of them to which hydrogen gas is added, in total pressure of 2 atmospheric pressure or less under compressive stress of 0.1 MPa or more in a temperature range of 1200 °C or less. Further, at the time of sintering, all the powder does not necessarily need to be nitrified and, for example, pure iron powders as a sintering-promoting agent may be mixed with. Furthermore, in the case of using steel powder whose grain size is 20 μm or less, in order to present grain growth suppressing effect, ceramic powders of TiN and TiC whose grain size is 2 μm or less can be added to steel powders.

An ultra fine grain steel having a nitride layer in accordance with the present invention is given not only high strength and high toughness but also high

fatigue strength and excellent wear resistance and hence is expected to be put into practical use as a material expanding an application field to various kinds of molded parts, parts, and members.

Table 1

(a) Coarse grain steel

Material		C	Si	Mn	P	S	Ferrite grain size (μm)
Fe-C-Mn	0.002C	0.002	0.01	1.98	0.001	0.002	20.0
Fe-C-Mn-Si	0.25C	0.27	0.23	0.37	0.008	0.030	20.0
	0.45C	0.43	0.22	0.83	0.017	0.016	—

(b) Ultra fine grain steel

Material		C	Si	Mn	P	S	Ferrite grain size (μm)
Fe-C-Mn	0.05C	0.05	0.01	1.98	0.021	0.001	1.7
Fe-C-Mn-Si	0.15C	0.14	0.31	1.51	0.001	0.001	0.5
	0.45C	0.43	0.31	1.50	0.001	0.001	0.7
	0.76C	0.76	0.31	1.43	0.012	0.004	0.5
	0.90C	0.89	0.30	1.51	0.002	0.001	0.5
	0.15C-0.1P	0.14	0.30	1.48	0.093	0.001	0.6
	0.45C-0.1P	0.45	0.30	1.49	0.100	0.001	0.5

Examples

In Table 1 are shown chemical components and ferrite grain sizes of materials used in examples and in Table 2 are shown mechanical properties. Each of the Fe-C-Mn coarse grain steel containing 0.002 mass % C and the Fe-C-Mn-Si coarse grain steel containing 0.25 mass % C has a ferrite grain size of about 20 μm and has a ferrite pearlite structure. The Fe-C-Mn-Si coarse grain steel containing 0.45 mass % C has a tempered martensite structure. The ultra fine grain steel has a ferrite structure in which fine ferrite grains and carbides are dispersed. The ultra fine grain steel was formed into a square bar of 18 mm \times 18 mm by rolling with grooved rolls.

Table 2

(a) Coarse grain steel

Material		Tensile strength (MPa)	Total elongation (%)	Vickers hardness
Fe-C-Mn	0.002C	—	—	114
Fe-C-Mn-Si	0.25C	511	34	155
	0.45C	706	25	230

(b) Ultra fine grain steel

Material		Tensile strength (MPa)	Total elongation (%)	Vickers hardness
Fe-C-Mn	0.05C	645	13	216
Fe-C-Mn-Si	0.15C	842	17	286
	0.45C	952	17	300
	0.75C	1143	12	360
	0.90C	—	—	364
	0.15C-0.1P	926	13	308
	0.45C-0.1P	1048	15	339

As shown in Table 2, in the Fe-C-Mn ultra fine grain steel containing 0.05 mass % C and Fe-C-Mn-Si coarse grain steel containing 0.15 mass % C, 0.45 mass % C, 0.75 mass % C, and 0.90 mass % C, as shown in Figs. 9(a) and 9(b), grain-shaped carbides increase with the amount of carbon and hence tensile strength and Vickers hardness increase by precipitation strengthening of carbides. In the Fe-C-Mn-Si ultra fine grain steels containing 0.15 mass % C and 0.1 mass % P and Fe-C-Mn-Si ultra fine grain steels containing 0.45 mass % C and 0.1 mass % P, as compared with the P-added ultra fine grain steel containing the same amount of C, tensile strength and Vickers hardness are larger. This is due to the solid solution strengthening of P.

The Fe-C-Mn coarse grain steel containing 0.002 mass % C and the Fe-C-Mn ultra fine grain steel containing 0.05 mass % C were nitrified by plasma under a condition of 550 °C × 26 hours. Fig. 1 is an FE-SEM photograph showing a nitride layer structure of the Fe-C-Mn coarse grain steel containing 0.002 mass % C. It can be seen from this FE-SEM photograph that streaky nitrides are formed in

ferrite grains.

Fig. 2 is a bar graph showing Vickers hardness of a raw material and a surface of a nitride layer of the Fe-C-Mn coarse grain steel containing 0.002 mass % C and the Fe-C-Mn ultra fine grain steel containing 0.05 mass % C. Vickers hardness was measured by applying a load of 1 kg onto a surface of a plate which was nitrified by plasma and has a thickness of 1 mm. It can be seen that even the Fe-C-Mn steel having a simple composition is hardened by nitrifying and that the ultra fine grain steel is more heavily hardened by nitrifying.

Fig. 3 is a graph showing hardness distribution after nitrifying of a fatigue test piece of the Fe-C-Mn ultra fine grain steel containing 0.05 mass % C. The nitrifying was performed by plasma under a condition of $550\text{ }^{\circ}\text{C} \times 26\text{ hours}$ and a fatigue test piece was formed into a shape of a sand clock having a diameter ϕ of 6 mm at a test portion. Vickers hardness was measured in a state where a load of 0.2 kg is applied to the test piece. From the hardness distribution shown in Fig. 3, a nitride layer is estimated to be about 1mm in depth. Moreover, it is recognized that hardness of a matrix after nitrifying is lower than a raw material before nitrifying. This is because the matrix is coarsened at the time of nitrifying. Actually, as can be seen from Fig. 4 that is a FE-SEM photograph showing a matrix structure after nitrifying, the ferrite grains were coarsened to a size of from 5 μm to 10 μm .

Fig. 5 is a graph showing hardness distribution after nitrifying of a Fe-C-Mn-Si coarse grain steel containing 0.25 mass % C and 0.37 mass % Mn (circular bar having a diameter of 16 mm) which was subjected to nitrifying under a conditions of $500\text{ }^{\circ}\text{C} \times 16\text{ hours}$. Fig. 6 is a graph showing hardness distribution after nitrifying of a Fe-C-Mn-Si coarse grain steel containing 0.45 mass % C and 0.83 mass % Mn (circular bar having a diameter of 16 mm) which was subjected to nitrifying under a condition of $500\text{ }^{\circ}\text{C} \times 16\text{ hours}$. As is the case with pure iron,

in the coarse grain steel containing 0.25 mass % C and 0.37 mass % Mn, hardness is high at a surface but is not high inside. To the contrary, in the Fe-C-Mn-Si coarse grain steel containing 0.45 mass % C and 0.83 mass % Mn, it is recognized that inside hardness increases and a nitride layer whose depth is about 1 mm is formed. It is understood that the Fe-C-Mn-Si steel can be also nitrified. Moreover, as shown in Table 1, in all other coarse grain steels and ultra fine grain steels, the amount of Mn is 1.43 mass % or more and a nitride layer having depth of about 1 mm was formed. Therefore, it is understood that in the Fe-C-Mn or Fe-C-Mn-Si ultra fine grain steel having a simple composition, the necessary amount of Mn is more than 0.37 mass % so as to form a deep effective nitride layer, that is, hardened layer.

Fig. 7 is a graph showing results of fatigue tests of a raw material and a nitrified material of the Fe-C-Mn ultra fine grain steel containing 0.05 mass % C in comparison with each other. In the fatigue tests, a Clauze type rotary bending fatigue test apparatus and a test piece shaped like a sand clock and having a test portion of 6 mm of diameter ϕ were used. Here, with respect to the nitrified material, its surface was removed about 0.1 mm by grinding to remove defects introduced at the time of nitrifying. As can be seen from Fig. 7, the nitrified material had fatigue strength enhanced greatly as compared with the raw material though its matrix was coarsened, and a fatigue limit of the raw material was 375 MPa whereas a fatigue limit of the nitrified material was 640 MPa. The hardness of the matrix of the nitrified material is about HV 160 and hence by use of an experimental formula of

$$\text{Fatigue limit} = 1.6 \times \text{Vickers hardness},$$

a fatigue limit of the base material is estimated to be $1.6 \times 160 = 256$ [MPa].

Assuming that the thickness of the nitride layer is 1 mm, and considering a stress gradient in a rotary bending test of the test piece having a diameter ϕ of 6 mm

(radius of 3 mm), a stress amplitude σ_a' applied to a portion just below the nitride layer becomes $\sigma_a'/\sigma_a = (3-1)/3 \approx 0.67$ where σ_a is a nominal stress amplitude at the surface. Therefore, the fatigue limit estimated from the hardness of the matrix and the stress gradient is about $256/0.67 = 382$ [MPa], but the fatigue limit of the actual nitrified material is 640 MPa as described above. It is recognized that the nitrified material has much more enhanced fatigue strength as compared with a fatigue limit expected from the hardness of the matrix. If the same estimation as described above is done by use of the fatigue limit of 376 MPa measured on the raw material, from the result shown in Fig. 3, a nitrifying depth showing the same hardness as that of the raw material is about 0.6 mm and $\sigma_a'/\sigma_a = (3-0.6)/3 = 0.8$, so that the predicted fatigue limit of the nitrified material is $375/0.8 = 469$ [MPa]. It is understood that the actual fatigue limit of 640 MPa of the nitrified material is larger than the predicted value.

As described above, in an ultra fine grain steel, even if grains are coarsened in some degree by nitrifying, a large effect of nitrifying with respect to fatigue strength is obtained. However, when considering actual parts and members, it is desirable that even if a base material is nitrified, it keeps an ultra fine grain structure and retains strength.

Then, results of examination on a grain growth suppressing effect by Fe_3C are shown in Fig. 8. Specifically, a fatigue test piece made of a Fe-C-Mn-Si based ultra fine grain steel and having a test portion of 6 mm in diameter was held at 500 °C for 30 hours by use of an ordinary electric furnace so as to simulate a nitrifying process performed at high temperature for a long time and then a change in hardness of the test piece was measured. As shown in a graph of Fig. 8, in the ultra fine grain steel containing 0.05 mass % C and the ultra fine grain steel containing 0.15 mass % C, when they were held at high temperature for about 3 hours, hardness decreased to about Hv 200 and grain coarsening was recognized.

In contrast with the fact, hardness of the ultra fine grain steel containing 0.45 mass % C decreases slightly and a sign of grain coarsening was not shown though it was held at high temperatures for 30 hours. Also, in the ultra fine grain steel containing 0.75 mass % C and the ultra fine grain steel containing 0.90 mass % C, the same results were obtained.

Figs. 9(a) and 9(b) are FE-SEM photographs showing a base material structures before nitrifying of the Fe-C-Mn-Si ultra fine grain steel containing 0.15 mass % C and the Fe-C-Mn-Si ultra fine grain steel containing 0.45 mass % C, respectively. Many Fe_3C s (white speckles) precipitated in the Fe-C-Mn-Si ultra fine grain steel containing 0.45 mass % C. It is estimated that grains of the Fe-C-Mn-Si ultra fine grain steel containing 0.45 mass % C were not coarsened by grain growth suppressing effect of the Fe_3C precipitates. Moreover, it was recognized that ferrite grain size was 1 μm or less in both of the ultra fine grain steels.

Fig. 10 is a graph showing a grain growth suppressing effect in the ultra fine grain steel containing 0.15 mass % C and 0.1 mass % P. As can be seen from Fig. 10, in the ultra fine grain steel containing 0.15 mass % C and 0.1 mass % P, hardness decreased slightly as compared with the ultra fine grain steel containing 0.15 mass % C and hence grain coarsening was suppressed. The cause is estimated to be grain growth suppressing effect by solid solution of P.

From the results described above, it is concluded that the grain growth suppressing effect of a carbide or solid solute element prevents or suppresses grain coarsening to maintain an ultra fine grain structure and that nitrifying of a long time is possible while preserving high strength.

In order to further examine effectiveness of nitrifying a ultra fine grain steel by use of the grain growth suppressing effect, a Fe-C-Mn-Si ultra fine grain steel containing 0.45 mass % C that utilizes Fe_3C precipitates, a Fe-C-Mn-Si ultra

fine grain steel containing 0.15 mass % C and 0.1 mass % P that utilizes solid solution of P, and a Fe-C-Mn-Si based ultra-refined steel containing 0.45 mass % C and 0.1 mass % P that utilizes both of the Fe_3C precipitate and the solid solution of P were actually nitrified and the fatigue test was conducted. The nitrifying was performed by plasma under a condition of $500\text{ }^{\circ}\text{C} \times 16\text{ hours}$. In the fatigue test, stepwise tests one unit of which was 107 tests per one test piece having a test portion of 6 mm in diameter and formed into a shape of a sand clock were conducted by use of the Clauze type rotary bending test apparatus and only fatigue limits were measured. Fig. 11 is a graph showing hardness distribution of the Fe-C-Mn-Si ultra fine grain steel containing 0.45 mass % C and 0.1 mass % P which was subjected to the nitrifying. As can be seen from the graph shown in Fig. 11, in the Fe-C-Mn-Si ultra fine grain steel containing 0.45 mass % C and 0.1 mass % P and subjected to the nitrifying, even a matrix shows about Hv 300 and an ultra fine grain structure is held. The fatigue test results of the respective nitrified materials are shown in Table 3.

Table 3

		Fatigue limit (MPa)		
		0.45C	0.15C-0.1P	0.45C-0.1P
Fe-C-Mn-Si steel	Raw material	500	520	580
	Nitrified material	700	780	700

The fatigue limits after nitrifying were 700 MPa for the ultra fine grain steel containing 0.45 mass % C, 780 MPa for the ultra fine grain steel containing 0.15 mass % C and 0.1 mass % P, and 700 MPa for the ultra fine grain steel containing 0.45 mass % C and 0.1 mass % P. As shown in Table 2, the Vickers hardness of the matrixes of the respective steels are 300, 308, and 339, so that the

ratios of fatigue limit/Vickers hardness of a matrix are 2.33, 2.53, and 2.06 and all of them are larger than 1.6.

By the way, fatigue fracture started from a surface in the ultra fine grain steel containing 0.45 mass % C and the ultra fine grain steel containing 0.15 mass % C and 0.1 mass % P, whereas fatigue fracture started from inside inclusions in the ultra fine grain steel containing 0.45 mass % C and 0.1 mass % P. It is understood from these facts that an intrinsic fatigue limit of the nitrified structure was obtained in the ultra fine grain steel containing 0.45 mass % C and the ultra fine grain steel containing 0.15 mass % C and 0.1 mass % P but that a fatigue fracture decreases in the ultra fine grain steel containing 0.45 mass % C and 0.1 mass % P because fatigue fracture starts from the inclusions. It is expected that if the inclusions are reduced in size, for example, by use of a cleaning technology to prevent fatigue fracture starting from the inclusions, the ultra fine grain steel containing 0.45 mass % C and 0.1 mass % P can provide a fatigue limit beyond 780 MPa of the ultra fine grain steel containing 0.15 mass % C and 0.1 mass % P because the ultra fine grain steel containing 0.45 mass % C and 0.1 mass % P has higher hardness.

As hardness becomes higher, wear resistance becomes more excellent. As shown in Fig. 2, difference in hardness between the raw material and the nitride layer is twice or more larger in the ultra fine grain steel than in the coarse grain steel. In other words, if an ultra fine grain steel is nitrified, increase of hardness of the ultra fine steel is more than that expected for a coarse grain steel and hence the ultra fine grain steel has excellent wear resistance. Moreover, from the comparison between Fig. 2 and Fig. 11, it is expected that since precipitation of carbide such as Fe_3C and addition of solid solute element such as P can increase hardness of a nitride layer by precipitation strengthening and solid solution strengthening, more enhancement of wear resistance will be estimated.

In addition, as shown in Fig. 8, Fig. 10, and Fig. 11, grains do not grow at a nitrifying temperature. It is thought from this fact that even if heat is generated by friction, an ultra fine grain structure can be maintained against temperature increase at a frictional surface up to around nitrifying temperature, decrease of strength will be zero or small, and excellent wear resistance can be obtained.

Of course, the present invention is not limited to the above-described embodiments and examples. Needless to say, the invention can be modified in the details such as chemical components of steel, nitrifying conditions, and nitrifying method.

Industrial Applicability

As described above in detail, the present invention can provide an ultra fine grain steel having a nitride layer that is formed without adding alloy elements such as Cr and Mo, which are expensive and detrimental at the time of recycling, and the steel whose fatigue strength is enhanced.